Ab initio prediction of electron and phonon transport in single-molecule junctions

M. Blaschke[1], **L. Martin**[1], **and F. Pauly**[1]

[1]*Institute of Physics and Centre for Advanced Analytics and Predictive Sciences, University of Augsburg, 86135 Augsburg, Germany*

E-mail: Matthias.Blaschke@uni-a.de

Universität Augsburg University

Background

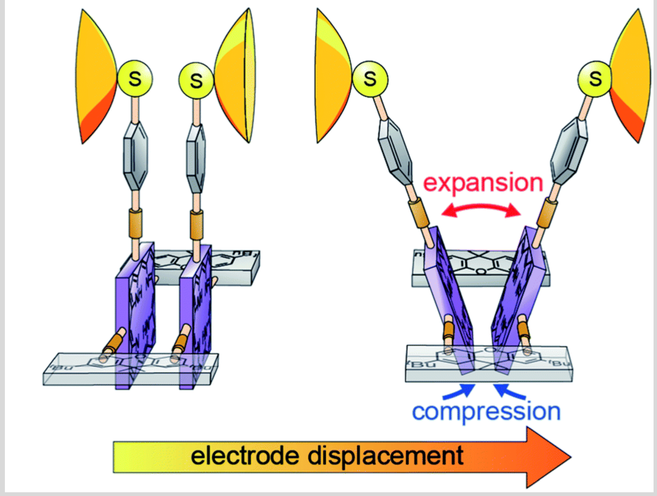

Figure taken from [7]

- **Molecular Electronics**: Single molecules serve as electronic components when contacted by macroscopic electrodes
- **Circuit Design via Chemistry**: Aiming at creating functional circuits through precise chemical design
- **Fundamental research on transport mechanisms:** Single-molecule junctions are ideal test platforms
- **New Functionalities:** Transport properties influenced by quantum effects allow for novel applications

Electron transport description

- **Landauer formalism:** Transmission $\tau(E)$ calculated by

$$\tau(E) = \mathrm{Tr}\left[\Gamma^r_{\mathrm{L}}(E) G^r_{\mathrm{C}}(E) \Gamma^r_{\mathrm{R}}(E) G^a_{\mathrm{C}}(E)\right]$$

$$G^r_{\mathrm{C}}(E) = \left[E S_{\mathrm{C}} - H_{\mathrm{C}} - \Sigma^r_{\mathrm{L}}(E) - \Sigma^r_{\mathrm{R}}(E)\right]^{-1}$$

$$\Sigma^r_{\mathrm{X}} = \left(H_{\mathrm{CX}} - E S_{\mathrm{CX}}\right) g_{\mathrm{X}}(E) \left(H_{\mathrm{XC}} - E S_{\mathrm{XC}}\right)$$

$$\Gamma_{\mathrm{X}}(E) = -2\mathrm{Im}\left[\Sigma^r_{\mathrm{X}}(E)\right]$$

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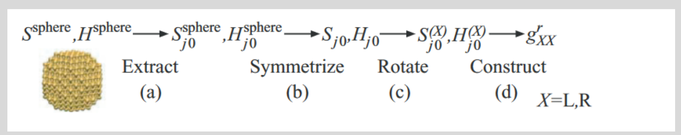
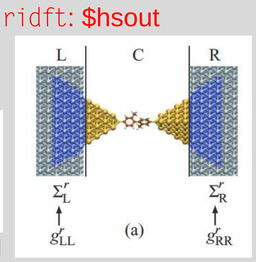
- **Cluster-based approach:** [4]

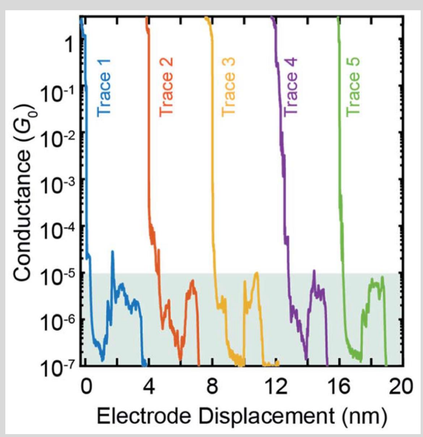


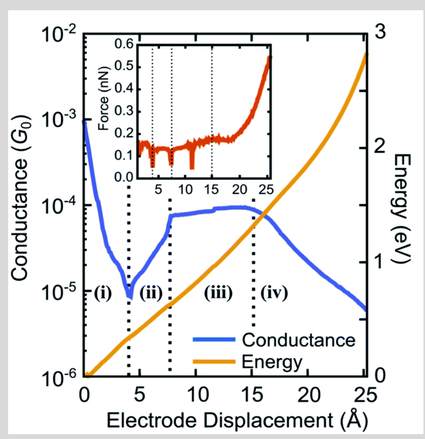
Figures taken from [4]



- **Derived electronic properties:** Conductance and thermopower

Electronic transport





Figures taken from [7]

- Good agreement between experimental data and theoretical prediction
- Rigorously tested and validated through an extensive record of collaborative experimental research [1,2,6-10]

Insight into transport mechanisms

- Decomposition into transmission eigenchannels and corresponding wave functions:

$$G = G_0 \sum_n \tau_n(E_{\mathrm{F}})$$

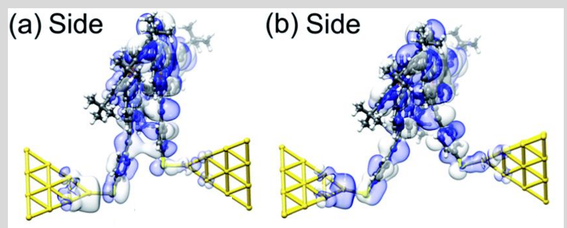
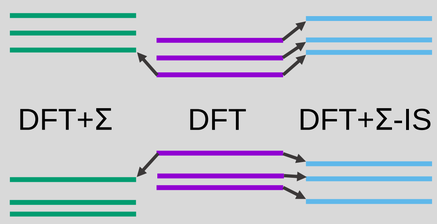


Figure taken from [7]

- Analysis shows crossover from through-space to through-bond transport

Corrections to DFT level alignment [6,7,8]



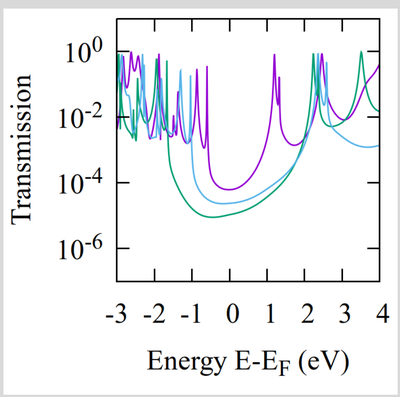


Figure taken from [8]

DFT+Σ: Uniform shift

$$\Sigma^{\mathrm{vrt}} = (-\mathrm{EA} - \epsilon_{\mathrm{L}}) - \Delta_{\mathrm{LUMO}}$$

$$\Sigma^{\mathrm{occ}} = \underbrace{(-\mathrm{IP} - \epsilon_{\mathrm{H}})}_{\text{molecular gap correction}} - \underbrace{\Delta_{\mathrm{HOMO}}}_{\text{image charge correction}}$$

DFT+S-IS: Individual shift

$$\Sigma^{\mathrm{vrt}}_i = (\epsilon^{G_0W_0}_i - \epsilon^{\mathrm{DFT}}_i) - \Delta_i$$

$$\Sigma^{\mathrm{occ}}_i = \underbrace{(\epsilon^{G_0W_0}_i + \epsilon^{\mathrm{DFT}}_i)}_{\text{molecular gap correction}} - \underbrace{\Delta_i}_{\text{image charge correction}}$$

Phononic Transport

- **Relevance**: Measurements of the thermal conductance of single-molecule junctions have only recently become possible [2]
- **Theoretical modeling:** Landauer formalism

$$\tau_{\mathrm{ph}}(E) = \mathrm{Tr}\left[\Lambda^r_{\mathrm{L}}(E) D^r_{\mathrm{C}}(E) \Lambda^r_{\mathrm{R}}(E) D^a_{\mathrm{C}}(E)\right]$$

$$D^r_{\mathrm{C}}(E) = \left[(E + i\eta)^2 - K_{\mathrm{C}} - \Pi^r_{\mathrm{L}}(E) - \Pi^r_{\mathrm{R}}(E)\right]^{-1}$$

$$\kappa_{\mathrm{ph}}(T) = \frac{1}{h} \int_0^\infty \mathrm{d}E E \tau_{\mathrm{ph}}(E) \frac{\partial n(E,T)}{\partial T}$$

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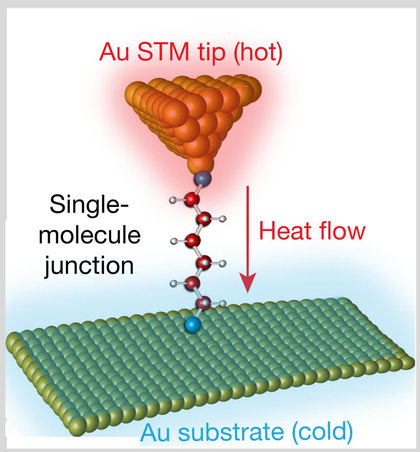
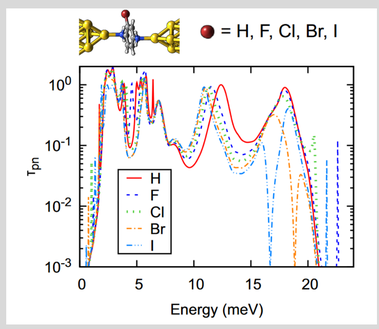
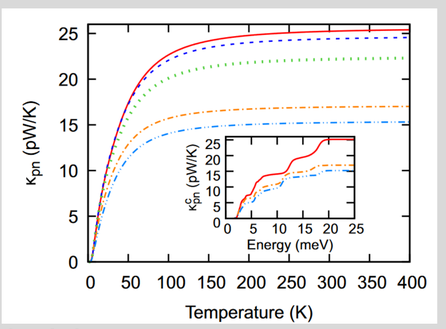


Figure taken from [2]





Figures taken from [11]

- Lattice contribution is the most relevant part of the thermal conductance for electrically rather insulating molecules
- Tools for calculation of phonon transmission and eigenchannel analysis available

Further computational tools and applications

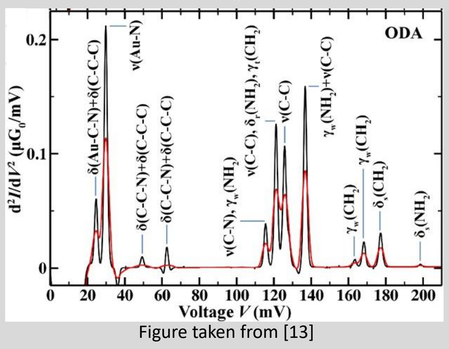


Figure taken from [13]

Inelastic electron tunneling (IET)

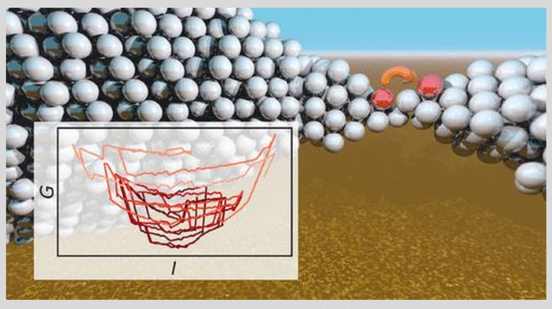


Figure taken from [14]

Current induced forces

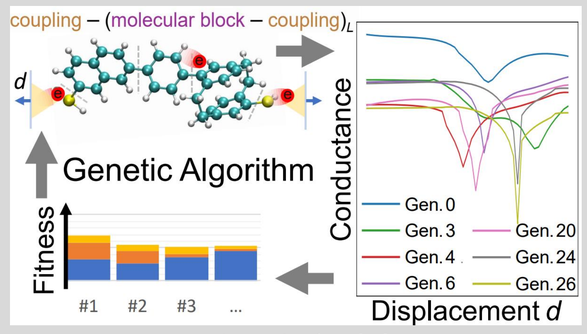


Figure taken from [15]

Molecular design: Tailor transport properties

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